

NICKEL OR NICKEL ALLOY ELECTROPLATING BATH AND ELECTROPLATING  
METHOD

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NICKEL OR NICKEL ALLOY ELECTROPLATING BATH AND ELECTROPLATING  
METHOD

[Nikkeru matawa nikkerugokin denkimekkiyoku oyobi denkimekkiho]

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Claims

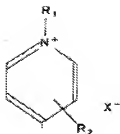
1. The nickel or nickel alloy electroplating baths posses the following constitution. /2\*
- (1) Nickel salts or nickel salts and at least one selected from water-soluble salts of boron, cobalt, copper, iron, manganese, phosphorus, tin, and zinc.
- (2) Quaternary ammonium compounds as brighteners which can be represented by any of general formulas [A]-[S]

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\* [Numbers in the margin represent pagination of the original foreign language text.]

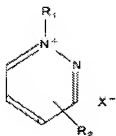
General formula [A]

[Structural formula 1]



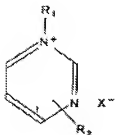
General formula [B]

[Structural formula 2]



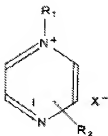
General formula [C]

[Structural formula 3]

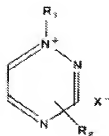


General formula [D]

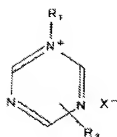
[Structural formula 4]



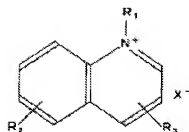
General formula [E]  
[Structural formula 5]



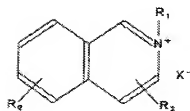
General formula [F]  
[Structural formula 6]



General formula [G]  
[Structural formula 7]

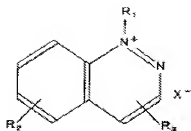


General formula [H]  
[Structural formula 8]



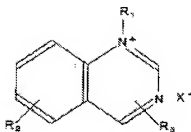
General formula [I]

[Structural formula 9]



General formula [J]

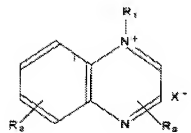
[Structural formula 10]



/3

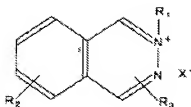
General formula [K]

[Structural formula 11]



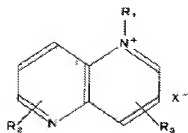
General formula [L]

[Structural formula 12]



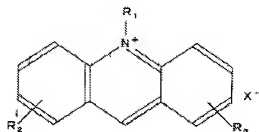
General formula [M]

[Structural formula 13]



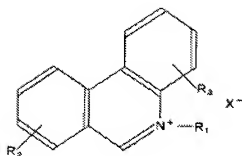
General formula [N]

[Structural formula 14]



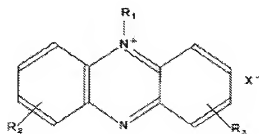
General formula [O]

[Structural formula 15]



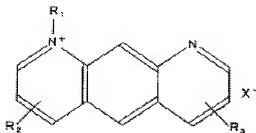
General formula [P]

[Structural formula 16]



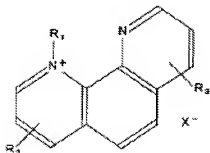
General formula [Q]

[Structural formula 17]



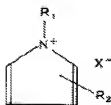
General formula [R]

[Structural formula 18]



General formula [S]

[Structural formula 19]



(wherein  $R_1$  is  $C_{6-18}$  alkyl group,  $R_2$  and  $R_3$  are at least one selected from – H, –  $CH_3$ , –  $C_2H_5$ , – OH, –  $OCH_3$ , –  $OC_2H_5$ , –  $NH_2$ , –  $NO_2$ , –  $COOH$ ,  $SO_3H$ , X is halogen ion, –  $CH_3SO_4^-$ ,  $C_2H_5SO_4^-$ ,  $CH_3COO^-$ , and  $NO_3^-$ ) as brighteners.

### 3. pH 3–pH 10

Nickel or nickel alloy electroplating methods, characterized by electroplating electronic components (parts) using the nickel or nickel alloy electroplating baths described in Claim 1.

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### Detailed description of the invention

[0001]

#### Application fields of the invention

The present invention relates to nickel or nickel alloy electroplating baths used in electroplating of electronic components (parts) and electroplating methods using the said electroplating baths.

[0002]

#### Prior art

For electronic components made of ceramics, glass, plastics, etc., usually tin or tin alloy plating is carried out for improving the solder wettability of electrodes. However, mostly nickel or nickel alloy plating is carried out on substrates for preventing solder encroachment and cracks.

[0003]

At this time various problems occur which do not occur when plating metals.

[0004]

In chip components which use glass and ceramics, in case chloride baths (pH about 2.0) are used in plating, glass and ceramics are severely corroded, and in case sulfamic acid or Watt baths (pH about 4.0) were used in plating, although glass and ceramics are not corroded, they (glass and ceramics), which are originally insulators, are plated as well.

[0005]

To deal with such a problem, previously nickel or nickel alloy baths (pH 4-6) have been used with extremely small electroplating (electric) current.

[0006]

#### Problems to be solved by the invention

However, minimization of electroplating current relates to the following problems A-C.

(A) Drop of productivity due to lengthening of electroplating time.

(B) Deterioration of properties of components due to long immersion.

(C) No deposition of metal occurs at a portion of electrodes.

The present invention was carried out in view of the above-mentioned problems and the purpose of the present invention is to provide (1) nickel or nickel alloy electroplating baths which do not corrode electronic components, and thus even when current density is increased, metals are not deposited on insulators and (2) electroplating methods.



[0007]

Means for solving the problems

Nickel or nickel alloy electroplating baths and electroplating methods of the present invention were completed for solving the above-mentioned problems. The nickel or nickel alloy electroplating baths of the first invention of the present patent all characterized in using baths containing (1) nickel salts or nickel salts and at least one selected from water-soluble salts of boron, cobalt, copper, iron, manganese, phosphorus, tin, and zinc, (2) quaternary ammonium compounds as brighteners which can be represented by any of above-mentioned general formulas [A]-[S] (wherein  $R_1$  is  $C_{6-18}$  alkyl group,  $R_2$  and  $R_3$  are at least one selected from  $-H$ ,  $-CH_3$ ,  $-C_2H_5$ ,  $-OH$ ,  $-OCH_3$ ,  $-OC_2H_5$ ,  $-NH_2$ ,  $-NO_2$ ,  $-COOH$ ,  $SO_3H$ ,  $X$  (halogen ion),  $-CH_3SO_4^-$ ,  $C_2H_5SO_4^-$ ,  $CH_3COO^-$ , and  $NO_3^-$ ), and (3) the pH of the electroplating baths is pH 3-10.

[0008]

And the second invention of the present patent which is a method for electroplating nickel or nickel alloy is characterized in using the above-mentioned nickel or nickel alloy electroplating baths to electroplating electronic components.

[0009]

Implementation of the invention

The nickel or nickel alloy electroplating baths of the first invention of the present patent have the above-mentioned constitution and the reason why they attain the object of the present invention is as follows:

Namely the following phenomena (1)-(2) were ascertained and further study was carried out on brighteners and as a result it was found that by adding quaternary ammonium compounds as brighteners, which can be represented by the above-mentioned general formulas which satisfy the following (a)-(b), to pH 3-10 nickel or nickel alloy electroplating baths, the deposition of metal on the above-mentioned insulators was suppressed remarkably.

[0010]

(1) The elution of ceramics which are materials constituting electronic components depends greatly on pH and the elution is remarkable especially at pH 2 or lower or pH 10 or higher.

(2) Deposition of metal on insulators increases with the increase of corrosion of insulators and the condition of deposition differs remarkably depending on the type of brighteners used.

[0011]

(a) Heterocyclic structure with nitrogen-containing five-membered ring or six-membered ring, and

(b) The alkyl groups which are bonded to nitrogen atoms are C<sub>6-18</sub> bulky alkyl groups.

[0012]

The detailed mechanism of the brightener shown in the first invention of the present patent that works as an effective surfactant in the above-mentioned problems is not clear, but it is believed that the structures of the following (1)-(2) can act to suppress the deposition of metal.

(1) The alkyl group which can be represented as R<sub>1</sub> has a certain size (at least 8 carbon atoms in case of linear alkyl groups and at least 6 carbon atoms in case of cyclic alkyl groups).

(2) The side-chain group which can be represented by R<sub>2</sub> and R<sub>3</sub> are composed of functional groups having small molecular weight so that nitrogen atoms can approach the substrate and surfactant molecules can gather closely and become adsorbent.

[0013]

The alkyl group which can be represented by R<sub>1</sub> is C<sub>6-18</sub>, preferably C<sub>12-16</sub>, and can be a linear, branched, or cyclic alkyl group. In case the number of carbon atom is less than 6, the suppression effect is lost, whereas when it is greater than 18 the water solubility is lost.

[0014]

If the side chain group which can be represented by R<sub>2</sub> and R<sub>3</sub> are functional groups having a small molecular weight the suppression effect cannot be impaired. As the molecular weight increases, the suppression effect decreases gradually.

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[0015]

Next, if a large amount of the above-mentioned brighteners is added, the decomposition from reduction becomes vigorous so the process control becomes complex, thus it is preferable that a rather small amount is added and that it is 0.01-1 g/L, more preferably 0.01-0.5 g/L.

[0016]

As to the fundamental baths to which the above-mentioned brighteners are to be added, the pH of the baths is 3-10 because of the following reasons (1)-(2).

(1) The corrosion of glass and ceramics is affected by the pH of the baths rather than the bath compositions.

(2) The deposition of metal on glass or ceramics can be suppressed by using the brighteners of the present invention.

[0017]

Next, the present invention will be further explained concretely using application examples. However, the present invention is not limited to these Application Examples.

[0018]

# Application Examples

Table 1 shows the composition, pH, and bath temperature (°C) of samples No. 1 - No. 14.

[0019]

Table 1

試料 No								pH	浴温 (°C)
1	硫酸ニッケル 330(g/l)	塩化ニッケル 45(g/l)	ホウ酸 38(g/l)	臭化セチルトリニウム G 5(g/l)				4.2	60
2	スルファミン酸ニッケル 300(g/l)	塩化ニッケル 8(g/l)	ホウ酸 30(g/l)	臭化ベンジルトリニウム O 5(g/l)				4.2	60
3	塩化ニッケル 300(g/l)	塩化アンモニウム 25(g/l)	ホウ酸 30(g/l)	臭化セチルトリニウム C 5(g/l)				5.8	45
4	硫酸ニッケル 330(g/l)	塩化リチウム 300(g/l)	コハク酸 40(g/l)	アンモニウム 70(g/l)	ジメチルアミンホ テ 1(g/l)	塩化一セチルトリニ ウム G 5(g/l)		6.0	55
5	硫酸ニッケル 340(g/l)	塩化ニッケル 30(g/l)	硫酸ニッケル 15(g/l)	硫酸ナリタ 2.0(g/l)	硫酸アンモニウ ム 5(g/l)	ホウ酸 30(g/l)	臭化セチルトリ ニウム C 5(g/l)	4.7	40
6	硫酸ニッケル 124(g/l)	新薬 50(g/l)	臭化ラウリルトリニ ウム O 5(g/l)					5.5	30
7	硫酸ニッケル 89(g/l)	塩化ニッケル 133(g/l)	ホウ酸 50(g/l)	硫酸第1級 50(g/l)	塩化一セチル トリニウム O 5(g/l)			3.5	55
8	スルファミン酸ニ ケル 800(g/l)	硫酸マグネ シウム 10(g/l)	ホウ酸 60(g/l)	塩化一セチルニ ウム 1.35-トリニウム O 5(g/l)				4.0	60
9	硫酸ニッケル 240(g/l)	塩化ニッケル 45(g/l)	ホウ酸 30(g/l)	臭化第1級 50(g/l)	塩化一セチル トリニウム O 5(g/l)			4.0	60
10	硫酸ニッケル 120(g/l)	塩化第1級 3(g/l)	クエン酸 60(g/l)	臭化第1級 20(g/l)	臭化一セチル トリニウム O 5(g/l)			6.0	40
11	硫酸ニッケル 263(g/l)	硫酸第1級 144(g/l)	ホウ酸 20(g/l)	臭化一セチル トリニウム O 5(g/l)				4.0	40
12	硫酸ニッケル 300(g/l)	ホウ酸 30(g/l)						2.0	60
13	硫酸ニッケル 330(g/l)	塩化ニッケル 45(g/l)	ホウ酸 38(g/l)					4.2	60
14	スルファミン酸ニ ケル 300(g/l)	塩化ニッケル 8(g/l)	ホウ酸 30(g/l)					4.2	60

Key: 1 Sample No.  
2 Bath temperature (°C)  
3 Nickel sulfate

- 4 Nickel chloride
- 5 Boric acid
- 6 Cetylpyridinium bromide
- 7 Nickel sulfamate
- 8 Benzylpyridinium bromide
- 9 Ammonium chloride
- 10 Cetylpycolinium chloride
- 11 Lithium chloride
- 12 Succinic acid
- 13 Aqueous ammonia
- 14 Dimethylamineborane
- 15 4-Hydroxy-1-laurylpyridinium chloride
- 16 Nickel formate
- 17 Cobalt sulfate
- 18 Ammonium sulfate
- 19 Cetylquinolinium chloride
- 20 Nickel acetate
- 21 Copper acetate
- 22 Laurylisoquinolinium bromide
- 23 Ferrous sulfate
- 24 1-Octylpyridazinium chloride
- 25 Manganese sulfate
- 26 1-Cetyl-1,3,5-triazinium chloride
- 27 Phosphorous acid
- 28 2-Laurylcinnolinium chloride
- 29 Stannous chloride
- 30 Citric acid
- 31 Glycine
- 32 Laurylacridinium bromide
- 33 Zinc sulfate
- 34 1-Laurylphenazinium bromide
- 35 \* Outside the scope of the present invention.

[0020]

The plating baths made of samples shown in Table 1 were used and electroplating was carried out on a (3Φ) 5 x 5 mm nickel single sheet having a baked-on lead glass by changing current density ( $A/dm^2$ ) and electroplating time (minutes). The corrosion of the lead glass and deposition of metal on the lead glass are shown in Table 2.

[0021]

In the corrosion of glass in Table 2, the symbol “O” means no apparent corrosion, the symbol “Δ” means slight corrosion was observed, and the symbol “X” means remarkable corrosion was observed. In plating (deposition) of metal on glass in Table 2, the symbol “O”

means almost no deposition (plating) of metal was observed, the symbol “Δ” means slight deposition (plating) of metal was observed, and the symbol “X” means remarkable deposition of metal was observed.

[0022]

Table 2

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① 試料 No	② 電流密度 (A/dm <sup>2</sup> )	③ メッキ時間 (min)	④ ガラス部の 浸漬	⑤ ガラス面の メッキ
1	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
2	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
3	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
4	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
5	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
6	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
7	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
8	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
9	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
10	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
11	0.1	120	○	○
	1.0	12	○	○
	2.0	6	○	○
*12	0.1	120	×	×
	1.0	12	△	×
	2.0	6	○	×
*13	0.1	120	○	○
	1.0	12	○	△
	2.0	6	○	×
*14	0.1	120	○	○
	1.0	12	○	△
	2.0	6	○	×

⑥ (\*は本発明の範囲外)

Key:	1	Sample No.
	2	Current density ( $A/dm^2$ )
	3	Plating time (minutes)
	4	Corrosion of glass
	5	Plating (deposition of metal on glass
	6	* outside the scope of the present invention.

[0023]

It is apparent from Table 2 that in the pH 2 acidic bath (chloride bath) of sample 12, in case the corrosion time was long, corrosion of glass and deposition of metal on the glass were observed. Compared to this, in weakly acidic baths such as sample 13 (Watt bath) and sample 14 (sulfamic acid bath) the corrosion of glass was suppressed but when the current density was increased, deposition of metal on the glass was observed.

[0024]

On the other hand in cases of baths shown by samples 1-11, even when the current density was increased, the corrosion of the glass and deposition of metal were not observed.

[0025]

Effect of the invention

When the present invention is used, electronic components are not corroded and even when the current density is high, metals are not deposited (electroplated) on insulators.